# Hydrogen Storage of Magnesium-Based Nanocomposites System

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Hydrogen storage in traditional metallic hydrides can deliver about 1.5 to 2.0 wt pct hydrogen but magnesium hydrides can achieve more than 7 wt pct. However, these systems suffer from high temperature release drawback and chemical instability problems. Recently, big improvements of reducing temperature and increasing kinetics of hydrogenation have been made in nanostructured Mg-based composites. This paper aims to provide an overview of the science and engineering of Mg materials and their nanosized composites with nanostructured carbon for hydrogen storage. The needs in research including preparation of the materials, processing and characterisation and basic mechanisms will be explored. The preliminary experimental results indicated a promising future for chemically stable hydrogen storage using carbon nanotubes modified metal hydrides under lower temperatures.

**KEY WORDS: Hydrogen storage; Magnesium; Nanocomposites; Catalytic effects; Transition metals; CNTs**

## 1. Introduction

Clean and sustainable energy conversion, storage and utilization are becoming increasingly important because of the rapid economic development and population growth, environmental pollution and greenhouse gas emissions[1] as well as national energy security. Hydrogen has been recognized as an ideal energy carrier in the twenty-first century for a clean-energy concept to achieve energy independence, reduction of greenhouse gases and other harmful emissions. A safe, economical and effective hydrogen storage system is critically needed for the future utilization of hydrogen. In 2003, a new concept for "Hydrogen Economy" has been presented by US government with a vision of "Hydrogen is American's clean energy choice. Hydrogen is flexible, affordable, safe and domestically produced, used in all sectors of the economy, and in all regions of the country"[2]. Despite these compelling benefits, realization of a hydrogen economy faces many challenges. US Department of Energy (DOE) has proposed a US$1.7 billion first-five-year plan to begin the development for hydrogen economy and its objectives that will be achieved in several decades. One of the five key R & D areas is hydrogen storage[2].

Compressed gas storage is the most commonly used method for hydrogen storage at present but requires the use of a heavy high strength container. Another way is liquid storage of hydrogen, which requires very low temperature of 20 K and efficient insulation. Hydrogen storage in solid-state matrix (*e.g.*, metal hydride) has the advantage of being very safe but the storage capacity of present materials is relatively low (about 1.4 wt pct). Furthermore, the storage systems are heavy and expensive. They are, therefore, limited in their applications in some niche areas such as portable power facilities and in fuel-cell electric vehicles (FCEV)[3] that are a priority in the hydrogen economy. Metal hydrides offer a safe alternative to storage in compressed or liquid hydrogen, and also have the highest storage capacity by volume[4] compared with all other storage methods. For application in FCEV, new materials with lighter elements have been investigated in recent years because it could overcome the disadvantages of heavy weight in conventional metal hydrides.

Following US hydrogen economy plan, many countries such as European countries, China, Japan, including Australia, have invested big funding on sustainable energy research and development. In Australia, great efforts are being carried out on hydrogen production by biomass (such as coal) gasification and gas separation (CSIRO Flagship), hydrogen storage by novel carbon materials such as carbon nanotubes and mesoporous carbon (ARC national research priority), fuel cells (ARC Federation Fellowship) *etc.* Recently, a novel technology has been applied to gasify bagasse (waste of sugar industry) for producing hydrogen in Australia. One of the most challenges is how to separate the gasified products (mainly composed of hydrogen and carbonic oxide) and store the hydrogen. Solid-state hydrogen storage materials such as metal hydrides are the most promising candidates for this specific purpose because the materials only adsorb hydrogen and release very high-purified hydrogen during desorption. Accordingly, the separation and storage of hydrogen for bagasse gasification could be perfectly solved concurrently if ideal hydrogen storage materials are developed. This specific application in sugar industry is thus concurred to the requirement of hydrogen storage materials in other promising areas.

## 2. Magnesium and Mg-based Alloys for Hydrogen Storage

With the increasing importance of hydrogen econ-

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omy, there is a great need for research to develop practical hydrogen storage systems. The main challenges in the field of hydrogen storage are to devise new materials or composites that exhibit: (1) high volumetric/gravimetric capacity[5], (2) fast sorption kinetics at low temperatures, (3) high stability with cycling, and (4) low costs and high operational safety standards. In recent years, a great deal of effort has been directed at research into metal or chemical hydrides as hydrogen storage materials[6].

Magnesium and Mg-based alloys are amongst the most attractive materials that could achieve the IEA targets for hydrogen storage because of their low cost and high capacity. With hydrogen, magnesium can form a hydride $MgH_2$ with a nominal 7.6 wt pct of hydrogen; a complex hydride $Mg_2FeH_6$ with the highest known volumetric hydrogen density of 150 $kgm^{-3}$, which is more than the double of liquid hydrogen[7]; and $Mg(BH_4)_2$ with a very high theoretical capacity about 14.8 wt pct hydrogen. However, magnesium-hydrogen materials are limited for practical application so far. The crucial limitations are: (1) Very high temperatures for hydrogenation and dehydrogenation. (2) Both hydrogenation and dehydrogenation reactions are very slow.

In practice, both adsorption and desorption of hydrogen require a temperature of at least 350~400°C and over a time scale of a few hours[8], which is impractical for FCEVs applications.

There are several factors that significantly hinder the rate of hydrogenation. One is the oxidation of Mg surface and/or formation of Mg hydroxide[9]. Oxide layers on the metal surface are normally impermeable to hydrogen molecules, preventing hydrogen molecules from transporting into the materials. Another reason for the very low rate of hydrogenation of Mg is the limited dissociation rate of hydrogen molecules into hydrogen atoms on the metal surface[10]. A clean surface of pure Mg is not active for the dissociation, however the dissociation barrier may be reduced by the presence of a catalytic metal such as Pd[11]. In addition, the hydrogenation rate of Mg is also influenced by the nucleation rate and growth of magnesium hydride which is dependent on hydrogen pressure. A higher pressure increases hydrogenation rate by increasing the thermodynamic driving force of the reaction[12].

## 3. Nanostructured Magnesium Hydrides

Nanoscale crystalline materials can provide extraordinary specific surface area and grain boundaries that can be very favourable for hydrogen adsorption and transport. Nanosized Mg particles can overcome the high energy barrier of hydrogenation encountered in bulk phase. Through nanostructuring, it would be possible for hydrogenation to occur at a low temperature with rapid kinetics. Recently, a breakthrough in hydride technology was brought about by the preparation of nanocrystalline hydrides with high-energy ball milling[13]. This method provides a good opportunity to improve hydrogen adsorption/desorption kinetics in several respects. Firstly, the breaking of surface oxide layers and the exposure of fresh Mg surfaces to hydrogen play a role in reducing the need for activation. The hydrogen-sorption kinetics is improved significantly by the microstructural changes in ball-milled Mg. Secondly, the grain size affects markedly hydrogen-sorption behaviour. The decreased crystallite size of the ball-milled Mg greatly increases the surface area of the Mg for hydrogen sorption. Further, the hydrogen reaction is limited by the growth of the hydride that is controlled by diffusion of hydrogen. The hydride layer on the surface of Mg is a barrier to this diffusion process. That is, the hydrogenation rate of the remaining Mg decreases with the increase of hydride layer thickness, and becomes virtually zero if the hydride layer exceeds a critical thickness. Due to its significantly increased surface to volume ratio, the nanocrystalline microstructure of the Mg overcomes this difficulty to exhibit good hydrogen-sorption kinetics. Thirdly, nanocrystalline Mg has an abundance of defects that act as nucleation sites for the hydride phase formation and large grain boundaries that facilitate hydrogen diffusion in the matrix[14]. The reduced crystallite size, increased specific surface area and the presence of defects induced by ball milling give rise to improved hydrogenation kinetics.

## 4. Magnesium-based Nanocrystalline Composites Doped with Nanoscale Catalysts

More recently, research on Mg-based nanocomposites for hydrogen storage is attracting much attention. Zaluski *et al.*[15] found that addition of Pd significantly increased the hydrogen adsorption/desorption kinetics. The Pd, served as catalyst, is uniformly distributed on the Mg surface in the form of nanoparticles in a very small quantity. The Pd particles remained unchanged during hydrogenation. In a search for cheaper catalysts than Pd, other metals were studied. It was found that Fe is also very effective, when introduced in the form of nanoparticles on the surface of Mg[16]. $MgH_2$-5 wt pct vanadium nanocomposite was also found to exhibit rapid hydrogenation kinetics where vanadium serves as a catalyst but needs more quantity compared with Pd additives[17].

Oelerich *et al.*[18] investigated the influence of metal oxides on the sorption behaviour of nanocrystalline $MgH_2$-based systems. It is found that the transition-metal oxides act as catalysts for the magnesium-hydrogen reaction. $Cr_2O_3$ yields the fastest hydrogen adsorption, whereas $V_2O_5$ and $Fe_3O_4$ cause the most rapid desorption of hydrogen. Yu *et al.*[19] investigated the hydrogen storage properties of nanocomposite $MgNi_2Cu_2$-$CrCl_3$ prepared by mechanical alloying to show very good kinetics of adsorption/desorption kinetics. In addition, exposure of the milled Mg-metal samples into air for 1 to 2 days, both the hydrogen sorption capacity and the kinetics are significantly improved to reveal that the oxygen played a unique role in the hydrogenation process[20]. However, the mechanisms of catalysis remain unclear

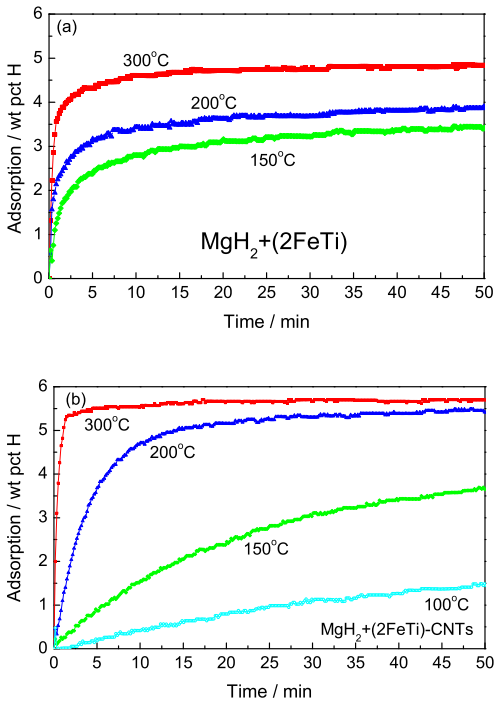


**Fig.1** Hydrogen adsorption of Mg-FeTi (a) and Mg-FeTi-$n$C (b) at different temperatures

## 5. Nanostructured Carbon ($n$C) Modified Mg-based Nanocomposites

Due to their high specific surface area and unique adsorbing properties, nanostructured carbons synthesized by hard templating method such as CMK-5 have been shown to have high catalytic dispersion and activity[21], and could be used for carrying nanoscale metal catalyst to be milled into $MgH_2$.

Carbon nanotubes have been extensively studied for hydrogen storage[22,23]. Both mesoporous carbons and carbon nanotubes have high surface area and consist of grapheme sheets. In our preliminary study, it was found that Mg-$n$C nanocomposites obtained by milling graphite with Mg had significantly increased capacity of hydrogen storage. For example, hydrogen adsorption of Mg-5 wt pct $n$C composites milled in a SPEX 8000 high-energy ball mill for 10 h, was measured at different temperatures[24]. The maximum capacity increased from about 5% to 6.8%. Additionally, the hydrogenation kinetics is also improved from 0.0172 wt pct/s to 0.0223 wt pct/s. However, only 1.33% and 0.6% of H was uploaded in 3000 s at 200°C and 150°C, respectively.

To improve the hydrogenation kinetics of the above composites, catalytic effect of some metals on hydrogen sorption was also investigated. Instead of noble elements as reported, two cheaper elements have been studied. Nanoscale Fe and Ti powders milled with $MgH_2$ remarkably enhanced the hydrogenation kinetics. The hydrogenation rates at 300, 200, 150°C reached 0.0712, 0.0427 and 0.0251 wt pct/s, respectively. As shown in Fig.1(a), hydrogen loading onto the composite reached 3.5%H and 3%H at 200 and 150°C within 15 min [25], which is significantly greater than those of the $MgH_2$-$n$C system.

However, it was observed that the maximum capacity of this system was only 5%H at 300°C, much lower than $MgH_2$-$n$C. It is hypothesized that $n$C and FeTi have different catalytic mechanisms: $n$C mainly increases the capacity, while FeTi highly enhances the kinetics. Assuming there is no interaction between FeTi and $n$C, addition of both $n$C and FeTi to the Mg-$H_2$ system is expected to improve both the maximum capacity and the hydrogenation kinetics. This is indeed the case as confirmed by the results shown in Fig.1(b). The maximum capacity for 200°C increased from 3.5 to 5.0%H and the hydrogenation rate is as fast as the system of $MgH_2$-5% (2FeTi). Even at a low temperature of 100°C, apparent hydrogen adsorption was observed (over 1%H within 15 min).

## 6. Conclusion

Magnesium and its alloys have a high capacity of more than 7 wt pct H and low costs, which might meets the goal for practical hydrogen storage, but limits to the sluggish kinetics. Control of composition and grain size as well as catalytic effect of different types of the catalysts, have been shown to be important in enhancing the hydrogenation kinetics of Mg-based materials. CNTs play a key role to increase the maximum capacity for hydrogen storage, and the combined metallic catalysts highly enhance the hydrogen sorption kinetics. The preliminary results are the most promising hydrogenation properties of Mg alloys so far and show that the practical hydrogen storage is certainly attainable. It is reasonable to expect that different nanoscale catalysts operate simultaneously to achieve a synergistic catalytic effect on hydrogen sorption.

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REFERENCES

[1 ] W.Oelerich, T.Klassen and R.Bormann: *J. Alloy. Compd.*, 2001, **315,** 237.

[2 ] *FY 2003 Progress Report,* Hydrogen, Fuel Cells and Infrastructure Tech., 2003.

[3 ] L.Schlapbach and A.Zuttel: *Nature,* 2001, **414,** 353.

[4 ] W.B.Fang, W.C.Zhang, Z.X.Yu and E.D.Wang: *The Chinese J. Nonferrous Metals,* 2002, **12,** 853.

[5 ] S.Louis: "Hydrogen in Intermetallic Compounds I", in: *Topics in Appl. Phys.,* Springe, Berlin, 1998, **63,** 350.

[6 ] L.Schlapbach and A.Zuttel: *Nature,* 2001, **414,** 353.

[7 ] A.M.Seayad and D.M.Antonelli: *Adv. Mater.,* 2004, **16,** 765.

[8 ] O.Gutfleisch, N.Schlorke-de Boer, N.Ismail, M.Herrich, A.Walton, J.Speight, I.R.Harris, A.S.Pratt and A.Zuttel: *J. Alloy. Compd.,* 2003, **356-357,** 598.

[9 ] F.D.Manchester and D.Khatamian: *Mater. Sci. Forum.*, 1988, **31,** 261.
[10] I.Zaluski, A.Zaluska, P.Tessier, J.O.Strom-Olsen and R.Schulz: *J. Alloy. Compd.*, 1995, **217,** 295.
[11] L.Schapbach: *Hydrogen in Intermetallic Compounds II,* ch. Surface properties and activation, Topics in Applied Physics, 1992.
[12] B.Vigeholm, K.Jensen, B.Larsen and A.Schroder-Pedersen: *J. Less-Commom Metals,* 1987, **131,** 135.
[13] I.Zaluski, A.Zaluska, P.Tessier, J.O.Strom-Olsen and R.Schulz: *Mater. Sci. Forum,* 1996, **225,** 853.
[14] L.E.A.Berlouis, E.Cabrera, E.Hall-Barientos, P.J.Hall, S.B.Dodd, S.Morris and M.A.Imam: *J. Mater. Res.*, 2001, **16,** 45.
[15] I.Zaluski, A.Zaluska, P.Tessier, J.O.Strom-Olsen and R.Schulz: *J. Alloy. Compd.*, 1995, **217,** 295.
[16] G.Bond: *Catalysis by Metals,* Academic Press, London and New York, 1962, Chap. **8,** 149.
[17] G.Liang, S.Boily, J.Huot, A.Van Neste and R.Schulz: *J. Alloy. Compd.*, 1998, **268,** 302.
[18] W.Oelerich, T.Klassen and R.Bormann: *J. Alloy. Compd.*, 2001, **315,** 237.
[19] Z.X.Yu, Z.Y.Liu and E.D.Wang: *J. Alloy. Compd.*, 2002, **333,** 207.
[20] G.Barkhordarian, T.Klassen and R.Bormann: *Scripta Mater.*, 2003, **49,** 213.
[21] S.H.Joo, S.J.Choi, I.Oh, J.Kwak, Z.Liu, O.Terasaki and R.Ryoo: *Nature,* 2001, **412,** 169.
[22] A.C.Dillon, K.M.Jones, T.A.Bekkedahl, C.H.Kiang, D.S.Bethune and M.J.Heben: *Nature,* 1997, **386,** 377.
[23] J.Lin: *Science,* 2000, **287,** 939.
[24] C.Z.Wu, X.Yao, C.Liu, D.M.Chen, H.M.Cheng and H.Wang: *National Conference on Hydrogen Energy,* November 2004, Beijing, China
[25] X.Yao, C.Z.Wu, H.Wang, H.M.Cheng and G.Q.Max Lu: submitted to *J. Alloy Compd.*, 2005.